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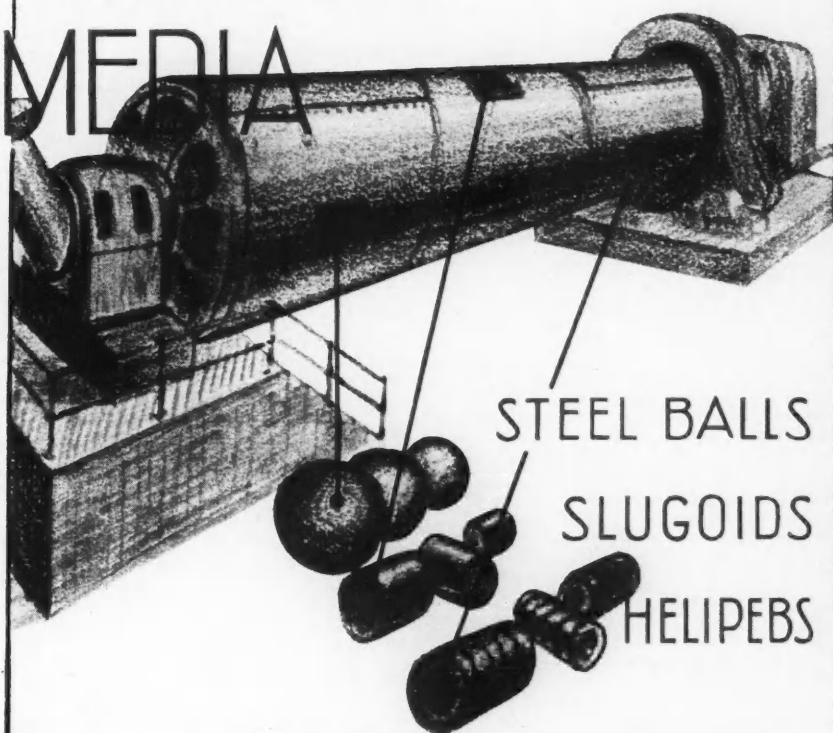
## MANUFACTURE

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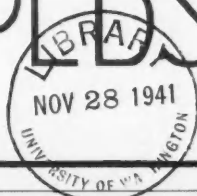
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## Effect on Clinker of Heat Treatment and Rate of Cooling.

A PAPER entitled "Effect of Heat Treatment and Cooling Rate on the Microscopic Structure of Portland Cement Clinker," by Mr. G. W. Ward, has been published as Research Paper No. 1358 by the United States National Bureau of Standards.

The various phases of the clinker are described in the following as they appeared in the etched polished surfaces when viewed microscopically by reflected light. *Figs. 1, 2 and 3*, although used to illustrate the typical appearance of all the clinkers tested after the various heat treatments, represent specifically the changes effected in one sample by slow, "plant," and quick cooling respectively.

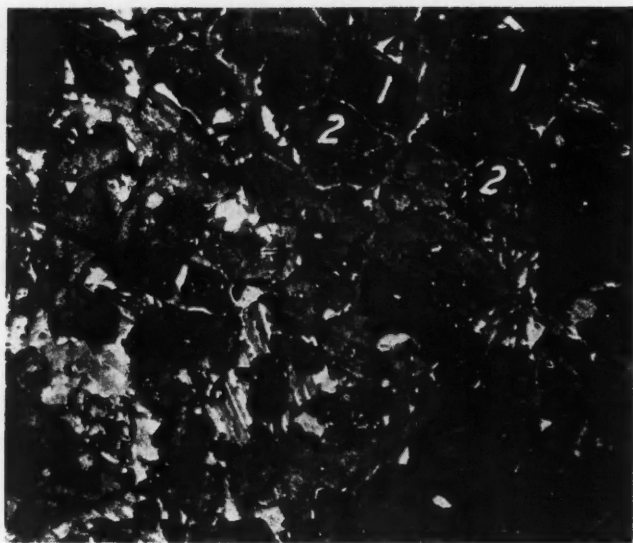
**Free Lime.**—Free lime ( $\text{CaO}$ ) etched readily after one minute's exposure in 1:3 water-alcohol solution. It appeared as dark grey, almost black, rounded or elliptical grains with no zoning, twinning, or inclusions. It occurred as inclusions in  $3\text{CaO} \cdot \text{SiO}_2$  and in the interstitial material. As the cooling became slower the amount of free lime decreased. In general, free lime was the first phase to crystallise. However, in slowly cooled clinkers, where the cooling occurred at a uniform rate from  $1,450$  to  $1,250$  deg. C. in about three hours, some of the free lime crystallised after  $3\text{CaO} \cdot \text{SiO}_2$ .

**Magnesia.**—Magnesia or periclase ( $\text{MgO}$ ) was observed without etching as brilliant crystals of high relief occurring well distributed throughout the interstitial material, and occasionally in slowly cooled and plant-cooled clinkers, as inclusions in  $3\text{CaO} \cdot \text{SiO}_2$ . As the cooling became slower crystal form became more prominent, octahedrons being found in slowly-cooled clinker. Cracking around the rims of the grains almost always occurred but tended to decrease in quickly-cooled clinkers, possibly because of the small crystal size in that type of



**Fig. 1.—Typical Slowly-cooled Clinker.**

1,  $3\text{CaO} \cdot \text{SiO}_2$ ; 2,  $\beta\text{—}2\text{CaO} \cdot \text{SiO}_2$ ; 3,  $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ ; 4,  $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$ ; 5,  $\text{MgO}$ . Distilled water and nitric acid etch. Magnification  $\times 500$ . Reflected light.

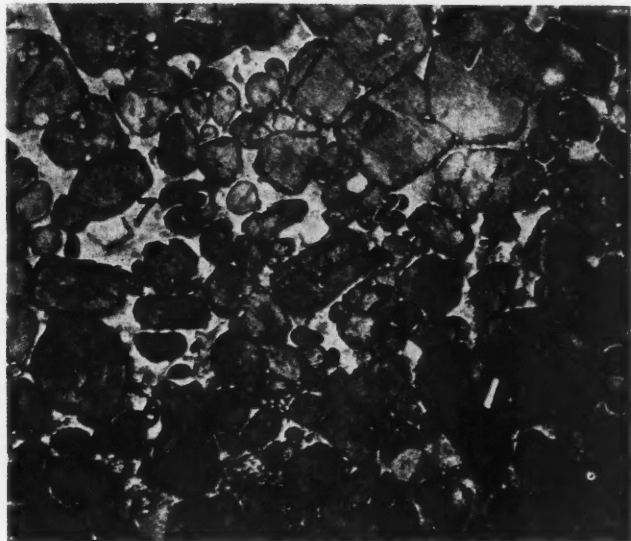


**Fig. 2.—Typical Plant-cooled Clinker.**

1,  $3\text{CaO} \cdot \text{SiO}_2$ ; 2,  $\beta\text{—}2\text{CaO} \cdot \text{SiO}_2$ ; 4,  $4\text{CaO} \cdot \text{Al}_2\text{O}_3$ ; 6, prismatic dark interstitial material, arrows indicate unknown phases. Note  $\beta\text{—}2\text{CaO} \cdot \text{SiO}_2$  rims around  $3\text{CaO} \cdot \text{SiO}_2$ . Distilled water and nitric acid etch. Magnification  $\times 500$ . Reflected light.

clinker. By actual measurement of many periclase particles, their average size was found to be greater in slowly-cooled than in plant-cooled clinkers, and larger in plant-cooled than in quickly-cooled clinkers.

**Tricalcium Silicate.**—Tricalcium silicate ( $3\text{CaO} \cdot \text{SiO}_2$ ) etched as dark grey, almost black, crystals after three to five seconds agitation in 1 per cent.  $\text{HNO}_3$ -alcohol mixture. Probably because of difference in orientation, a few crystals etched to a lighter colour. It was commonly the most abundant phase. In slowly-cooled clinkers it tended to be completely or partially included in tri-



**Fig. 3.—Typical Quickly-cooled Clinker.**

1,  $3\text{CaO} \cdot \text{SiO}_2$ ; 2,  $\beta$ - $2\text{CaO} \cdot \text{SiO}_2$ ; 5,  $\text{MgO}$ ; 7, glass and light interstitial material,  $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$ . Distilled water and nitric acid etch. Magnification  $\times 500$ . Reflected light.

calcium aluminate crystals. The development of good crystal form was observed to decrease with increased rate of cooling.

Re-solution of  $3\text{CaO} \cdot \text{SiO}_2$  and the resulting precipitation of  $\beta$ - $2\text{CaO} \cdot \text{SiO}_2$  were more prominent in slowly-cooled than in plant-cooled clinkers, and only very limited in quickly-cooled clinkers. This re-solution was indicated by embayed tricalcium silicate with dicalcium silicate occupying the bays and frequently by fringes of dicalcium silicate around tricalcium silicate.

The tendency to form twins or to be zoned decreased as the cooling became more rapid. Good examples of simple twinning were found in slowly-cooled and plant-cooled clinkers, with a greater number in the former. Zoning was well developed in the slowly-cooled clinker, with three or four zones not unusual, but it was developed to a lesser extent in the plant-cooled product and was rarely observed in quickly-cooled samples.

Inclusions of dicalcium silicate, magnesia, and free lime, sometimes accompanied by tetracalcium aluminoferrite, frequently occurred in tricalcium silicate irrespective of heat treatments. In a few instances periclase inclusions had dark halos, possibly indicative of solution in tricalcium silicate.

**Dicalcium Silicate.**—Beta-dicalcium silicate appeared without good crystal form, generally as spherical or elliptical crystals, which etched readily in 1 per cent. nitric acid-alcohol solution. Their distribution was generally good, but in some clinkers there was a strong tendency to form large groups. Commonly beta-dicalcium silicate occurred closely associated with tricalcium silicate as fringes, as inclusions, as pseudomorphs, or occupying embayments. In quickly-cooled clinkers, dicalcium silicate with complex twinning was the most frequently observed form of this phase. Occasionally, tetracalcium aluminoferrite appeared along twinning planes and in cracks. Simplicity of form, a general lack of inclusions, and fewer irregularities characterised the dicalcium silicate of quickly-cooled clinkers. In slowly-cooled clinkers dicalcium silicate untwinned, and with simple multiple twinning was more prominent. Frequently twinning extended out past the usually rounded-particle boundary to give a many-fingered appearance to the grain. It was not unusual for twinning to be indicated by an arrangement of small unidentifiable inclusions. Dicalcium silicate was often cracked radially and sometimes completely separated by cracking or embayment. The appearance of dicalcium silicate in plant-cooled clinker was characteristic of that found in either slowly- or quickly-cooled clinkers, since plant cooling was intermediate between these two cooling rates. Gamma-dicalcium silicate, sometimes in considerable amounts, was observed only in slowly-cooled clinkers.

#### Dark Interstitial Material.

Dark interstitial material consists of three types, namely, rectangular (identified as  $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ ), dark prismatic interstitial material, and glass.

Tricalcium aluminate ( $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ ) etched readily in freshly-distilled water to dark-grey rectangular masses, occasionally showing square outlines, and was often intimately associated with tetracalcium aluminoferrite. Where present it was distributed throughout the clinker structure and sometimes completely occupied the interstices. Roughly square or rectangular shapes were generally observed, but irregular areas appeared sometimes with the trace of one crystal face. There was no evidence of corrosion, twinning or zoning. The inclusions were dicalcium silicate, tricalcium silicate, and infrequently periclase. Small, scattered, bubble-like inclusions of what may be tetracalcium aluminoferrite occurred. Tricalcium aluminate was found in slowly-cooled clinkers when the  $\text{Al}_2\text{O}_3$ - $\text{Fe}_2\text{O}_3$  ratio was 1:63 or greater, and not in those of  $\text{Al}_2\text{O}_3$ - $\text{Fe}_2\text{O}_3$  ratio 0:97 or less. In the group studied, clinkers having  $\text{Al}_2\text{O}_3$ - $\text{Fe}_2\text{O}_3$  ratios between 0:97 and 1:63 were not available. Only two of the plant-cooled clinkers contained tricalcium aluminate. One of these had an  $\text{Al}_2\text{O}_3$ - $\text{Fe}_2\text{O}_3$  ratio of 1:89 and a low total alkali content (0.22 per cent.). The other had an  $\text{Al}_2\text{O}_3$ - $\text{Fe}_2\text{O}_3$  ratio of 2.91, the highest in this group, and a total alkali content of 1.00 per cent. In this latter case only a small percentage of the tricalcium aluminate calculated to



be present at crystalline equilibrium appeared. In quickly-cooled clinkers tricalcium aluminate was not found.

Prismatic dark interstitial material when etched in freshly-distilled water appeared as dark-grey, almost black, elongated crystals, frequently with darkened edges. It showed no corrosion, twinning or zoning. Occasionally the crystals were bordered by ragged, weakly etched dark interstitial material which was identified as glass. Scattered crystals and aggregates appeared throughout the clinker as slender, needle-like, and large, poorly-terminated crystals. Frequently they terminated against silicates. In thin sections viewed with transmitted light these crystals were anisotropic with a birefringence of about 0.01 and parallel extinction. Their refractive indexes were close to 1.72. Prismatic dark interstitial material was much more abundant in plant-cooled than in slowly- or quickly-cooled clinker. The quantity of this constituent appeared to be influenced by the rate of cooling. The high glass content of quickly-cooled clinkers indicated that rapid cooling prevents crystallisation of prismatic dark interstitial material, since this compound is one of the last to crystallise. This phase was more frequent in occurrence and better in development for high  $\text{Al}_2\text{O}_3$ - $\text{Fe}_2\text{O}_3$  ratio clinkers containing appreciable amounts of  $\text{Na}_2\text{O}$  and  $\text{K}_2\text{O}$  either alone or together.

Glass is revealed by etching with 10 per cent. KOH. The etchability of glass in other reagents depends on its composition. For instance, glass low in iron is readily etched with water followed by 1 per cent.  $\text{HNO}_3$  in alcohol, and glass high in iron is unaffected by this method. The amount of glass varied greatly with different cooling rates. In slowly-cooled clinker it occurred infrequently and was seen edging prismatic dark interstitial material. In plant-cooled clinker it occurred as irregular areas, blobs, small veinlets, and frequently as a jagged sheath around dark prismatic crystals. Etched quickly-cooled clinkers revealed glass as ragged areas, blobs, and veinlets. Occasionally it had a roughly prismatic form due to prior crystallisation of tetracalcium aluminoferrite prisms. When in the form of blobs it frequently gave the light interstitial material a mottled appearance which made difficult its differentiation from tetracalcium aluminoferrite.

Tetracalcium aluminoferrite ( $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$ ) was unaffected by most etchants and appeared as light interstitial material intimately associated with dark interstitial material. In the clinkers investigated, tetracalcium aluminoferrite was the last crystalline phase to appear except in compositions of low  $\text{Al}_2\text{O}_3$ - $\text{Fe}_2\text{O}_3$  ratios, where the tricalcium aluminate gave every indication of having been the last phase to crystallise. In slowly-cooled clinkers well-developed prisms of tetracalcium aluminoferrite were easily recognised in thin sections. The prism forms varied with the  $\text{Al}_2\text{O}_3$ - $\text{Fe}_2\text{O}_3$  ratio—large, broad forms predominating in clinkers of low ratio and small needle-like forms in those of high ratio. There was very little change from the amber colour and slight pleochroism of the pure compound.

In quickly-cooled clinkers tetracalcium aluminoferrite appeared as long narrow prisms irrespective of the  $\text{Al}_2\text{O}_3$ - $\text{Fe}_2\text{O}_3$  ratio. It was also frequently found as dendritic growths in clinkers having low  $\text{Al}_2\text{O}_3$ - $\text{Fe}_2\text{O}_3$  ratios. The large broad

prisms found in slowly-cooled clinker were practically absent. In many cases the amber colour of this phase was darker and greener, while the pleochroism became more pronounced, which may have been due to solid solution with  $\text{MgO}$ . Insley and McMurdie pointed out from their studies that there must be less than 1 per cent. of  $\text{MgO}$  in solid solution in tetracalcium aluminoferrite.

## The Hydration of Magnesia in Dolomitic Limes.

SOME notes on the desirability of hydrating the magnesia in dolomitic limes are given by Mr. T. C. Tayler in a recent number of *Pit and Quarry*, from which the following is taken. Dolomitic limestone of 60 per cent.  $\text{CaCO}_3$  and 40 per cent.  $\text{MgCO}_3$  content when burned becomes quicklime of 64 per cent.  $\text{CaO}$  and 36 per cent.  $\text{MgO}$  content. When water is added the  $\text{CaO}$  readily combines to form  $\text{Ca}(\text{OH})_2$ . Under ordinary hydrating conditions little or none of the  $\text{MgO}$  combines with water but it can be made to partly or fully combine to form  $\text{Mg}(\text{OH})_2$ . Thus ordinary hydrating methods give only 120.6 lb. of hydrate from 100 lb. of quicklime, whereas it is possible to get 136.8 lb.

Dolomitic lime fully hydrated makes as good sand-lime bricks as the high-calcium lime now generally used, and there are reasons to expect even better results. A sand-lime brick made with dolomitic lime containing unhydrated magnesia may increase in volume during hardening as much as 50 per cent. and will be worthless. It is important that there should be very little free  $\text{MgO}$  in lime used for sand-lime bricks.

Reports of the U.S. Bureau of Standards indicate that complete hydration of the magnesia increases the plasticity of the resultant mortar and plaster. A dolomitic lime not desirable for plastering may become a preferred product if it is fully hydrated.

For several decades the sand-lime-brick industry has fully hydrated magnesia, and *Fig. 1* shows a form of hydrator in general use to hydrate the magnesia in dolomitic lime. The machine consists of a steel drum built for 100 lb. steam

### Theoretical Combining Proportions

56 parts  $\text{CaO}$  + 18 parts  $\text{H}_2\text{O}$  = 74 parts  $\text{Ca}(\text{OH})_2$

40 parts  $\text{MgO}$  + 18 parts  $\text{H}_2\text{O}$  = 58 parts  $\text{Mg}(\text{OH})_2$

### Ordinary Hydration of 100 lb. of Dolomitic Quicklime

64 lb.  $\text{CaO}$  + 20.6 lb.  $\text{H}_2\text{O}$  = 84.6 lb.  $\text{Ca}(\text{OH})_2$

36 "  $\text{MgO}$  + 0 "  $\text{H}_2\text{O}$  = 36.0 "  $\text{MgO}$

100 " quicklime + 20.6 "  $\text{H}_2\text{O}$  = 120.6 " ordinary hydrate

### Complete Hydration of 100 lb. of Dolomitic Quicklime

64 lb.  $\text{CaO}$  + 20.6 lb.  $\text{H}_2\text{O}$  = 84.6 lb.  $\text{Ca}(\text{OH})_2$

36 "  $\text{MgO}$  + 16.2 "  $\text{H}_2\text{O}$  = 52.2 "  $\text{Mg}(\text{OH})_2$

100 " quicklime + 36.8 "  $\text{H}_2\text{O}$  = 136.8 " hydrate



pressure, mounted in trunnion bearings and revolved slowly to facilitate complete mixings of the contents. A measured batch, usually several tons, is fed into the machine, which is set in motion and a measured quantity of water is added through the trunnion. Hot or cold water or even steam may be supplied. Any excess

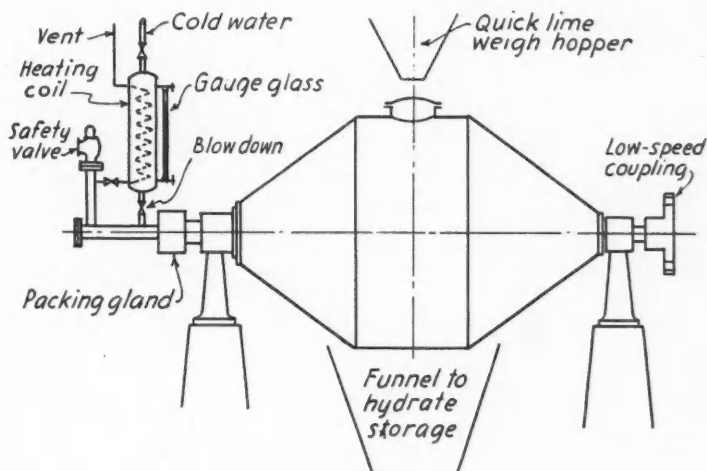


Fig. 1.—Hydrator for Magnesia in Dolomitic Lime.

of pressure generated is released through a safety valve. Blow-down steam may be used as indicated to preheat the water supply. The time required for complete hydration may vary from about 15 minutes to 90 minutes per batch, depending on several factors such as the steam pressure maintained, the temperature of the water supplied, the degree to which the lime has been burned, and the nature of the lime.

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## The Relationship of Grinding to Surface Measurement.

A STUDY of the theory of grinding as a phase of the problem of the measurement of the surface area of cement is given by Mr. S. S. Fritts (of the Lone Star Cement Corporation) in *Rock Products* for May 1941. The equation that forms the basis of this investigation is

$$y = ae^{-b/d} \quad (1)$$

where  $y = \log I_0 - \log I_d$ ,  $a$  = experimental constant,  $b$  = experimental parameter,  $e$  = Napierian logarithm base = 2.718, and  $d$  = diameter of particle in microns. Values for  $a$  and  $b$  may be determined analytically if  $y$  is known for any two values of  $d$ . Hence the parameter  $b$  may be found from the following:

$$b = \frac{2.303}{\frac{1}{d_2} - \frac{1}{d_1}} (\log \log I_{d_1} - \log \log I_{d_2}) \quad (2)$$

where  $d_1$  and  $d_2$  are particle sizes in microns, and  $\log \log I_{d_1}$  and  $\log \log I_{d_2}$  are the logs of the turbidimetric values corresponding to the particle sizes.

However, the better solution is by means of graphical methods, in which case equation (1) may be written

$$\log y = \log a - \frac{1}{2.303} \frac{b}{d} \quad (3)$$

By plotting values of  $\log$  turbidity or  $\log (\log I_0 - \log I_d)$  against  $1/d$  on semi-logarithmic paper and drawing a straight line through the points the values of the constant  $a$  and the parameter  $b$  are obtained. The intercept on the  $\log y$  axis is  $\log a$  and the slope is  $-0.4343b$ .

Calculation of surface area and particle size distribution based on equation (1) is rather long and tedious, and from a practical standpoint the application of the proposed law of turbidity versus particle size would be too involved. It has been found, however, that the mean particle size of the 0.75 micron fraction and the surface mean diameter for any limiting particle size bears a direct relation to the parameter  $b$  of equation (1). Thus it is only necessary to plot values of turbidity ( $\log I_0 - \log I_d$ ) against the reciprocal of the particle size on semi-logarithmic paper and determine the slope of the line from which the value of  $b$  is readily calculated. Fig. 1 shows the relationship between the mean particle size of the 0.75 micron fraction and the parameter  $b$ . This curve was prepared from the Table I and the calculations were based on an assumed normal distribution.

By means of the foregoing relation it is possible more nearly to approximate the actual mean diameter of the 0.75 micron fraction than that of the assumed mean diameter of 3.75 microns. It is of course necessary to make corrections in the Wagner equation to account for the change of the calculated particle size. The surface area is then given by:

$$S_{60} = \frac{38.1 \times \% \text{ minus } 325 \times (2 - \log I_{60})}{\Sigma (2 - \log I_d)} \quad (4)$$

where  $\Sigma (2 - \log I^a) =$

$$\begin{aligned} & 0.4 d_{m7.5} + (1.75 - 0.2 d_{m7.5}) \log I_{7.5} \\ & + 0.75 \log I_{10} + \log I_{15} + \log I_{20} \\ & + \log I_{25} \dots \dots \log I_{55} - 11.5 \log I_{60} \end{aligned}$$

and  $d_{m7.5}$  = mean particle size of (0-7.5) micron fraction.

Fig. 2 shows the relationship between the surface mean diameter of the material below the 325-mesh separation and the parameter  $b$ . Because of the uncertainty of the actual separation value of the 325-mesh sieve, curves have been prepared

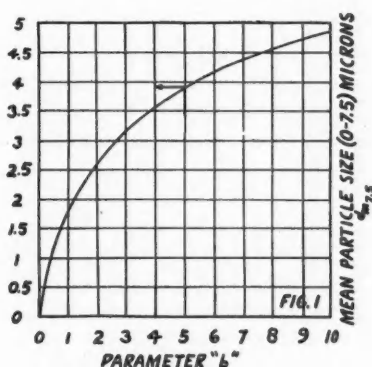


Fig. 1.—Relationship between Mean Particle Size (0-7.5 microns) and Parameter "b" of equation  $\gamma - ae = b/d$ .

TABLE I.

TABULATED VALUES OF MEAN PARTICLE SIZE (0-7.5) MICRON FRACTION AND PARAMETER "b".

Parameter "b"	Mean (0-7.5)
0.5	1.17
1.0	1.81
1.5	2.25
2.0	2.62
2.5	2.91
3.0	3.16
3.5	3.37
4.0	3.56
4.5	3.73
5.0	3.88
5.5	4.02
6.0	4.15
6.5	4.27
7.0	4.38
7.5	4.48
8.0	4.57
8.5	4.65
9.0	4.73
9.5	4.80
10.0	4.87

for the limiting particle sizes at 60, 55, 50, and 45 microns. These curves were prepared from Table II and the calculations were based on the same distribution function as applied to Table I. The total surface area of the material less than the 325-mesh separation is determined from the expression:

$$S_{325} = \frac{600 \times \% \text{ minus } 325}{\text{Sp. gr.} \times d_m} \quad \dots \quad (5)$$

For cements having a specific gravity of 3.15 the foregoing equation reduces to

$$S_{325} = \frac{190.5 \times \% \text{ minus } 325}{d_m} \quad \dots \quad (6)$$

The Wagner<sup>(1)</sup> equation for the determination of the surface area of cement is based on the assumption that the 325-mesh sieve separates at 60 microns. Experimental evidence<sup>(2,3)</sup> has indicated that the separation is nearly 45 microns or close to the aperture of the screen which is designated at 43 or 44 microns. In recent work it has been found that the 325-mesh sieve separates at 53 microns. Some laboratory-ground cements, commercial products, and crushed clinkers to the Portland Cement Association type of grindability<sup>(4)</sup> testing apparatus has shown a separation at 53 microns. Mathematically this means that the average

diameters of particles just passing a 325-mesh sieve with an opening of 44 microns on a side are equal to 1.207 times the sieve aperture. Or, in other words, the average diameter of particles just passing a sieve are equal to the mean between the inscribed and circumscribed diameters of the sieve aperture.

In order to test equation (1) or the proposed law of turbidity versus particle size, many turbimetric analyses were considered. However, for the purpose of examination, the plots of eleven samples of material are shown in Figs. 3 to 13. These materials cover a fineness range from the crushed clinker produced by the Portland Cement Association grindability testing apparatus to the fairly high-early-strength cements ground in open and closed circuit, as well as two types of cement raw materials. The particle size distributions, surface mean diameters and surface areas are shown in Table III, and are identified as follows. Sample

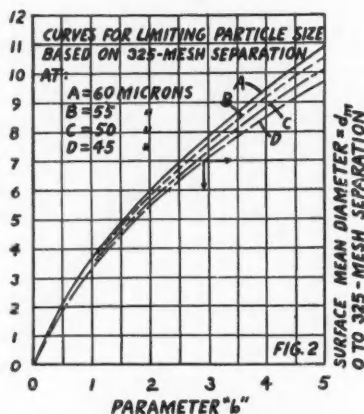


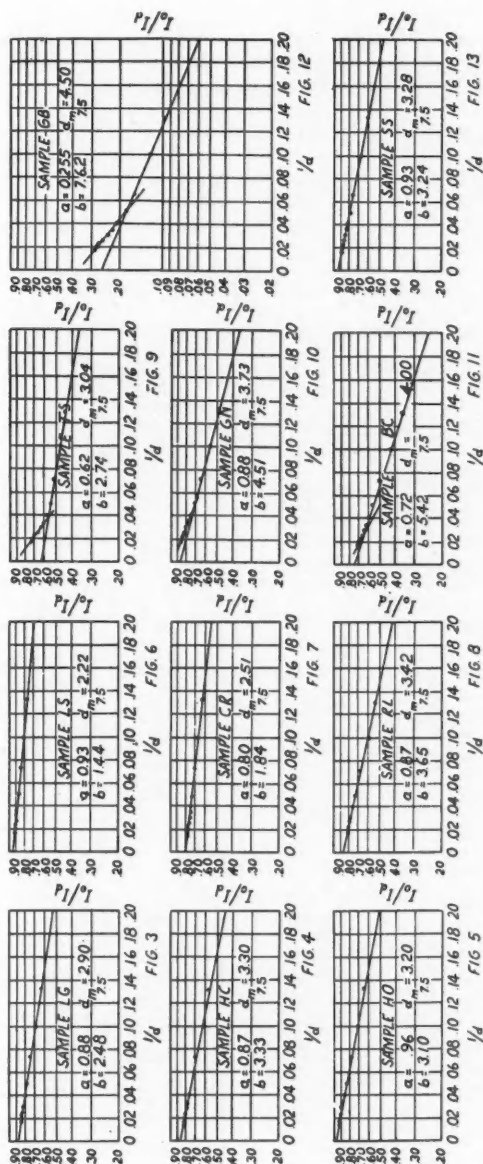
Fig. 2.—Relationship between Surface Mean Diameter and Parameter "b."

TABLE II.  
TABULATED VALUES OF  
SURFACE

Mean Diameters =  $d_m$  and Parameter "b"

Parameter "b"	Surface Mean Diameters at the Limiting Particle Sizes			
	60	55	50	45
0.5	2.13	2.09	2.05	1.99
1.0	3.63	3.55	3.46	3.36
2.0	5.98	5.83	5.66	5.47
3.0	7.85	7.62	7.38	7.11
4.0	9.46	9.17	8.85	8.51
5.0	10.89	10.53	10.15	9.73
6.0	12.17	11.75	11.30	10.82
7.0	13.34	12.87	12.36	11.81
8.0	14.41	13.88	13.32	12.71
9.0	15.40	14.82	14.20	13.53
10.0	16.32	15.70	15.02	14.29

LG.—A laboratory-ground clinker in a 12-in. by 12-in. batch-type tube mill. Dispersion effected by a modified procedure. Instrument calibrated by "mask" method. Sample HC.—A high-early-strength cement ground in closed circuit with air classifiers. Dispersion and instrument calibrated by standard method. Sample HO.—A high-early-strength cement ground in open circuit. Similar to sample HC. Sample LS.—A hard limestone ground in open circuit in a commercial-type combination tube mill. Dispersion effected in an aqueous solution with sodium silicate as a dispersing agent. Instrument calibrated by "mask" method. Time intervals by a stop watch calculated from viscosity-temperature relations for water. Specific gravity of material, 2.74. Sample CR.—A soft, argillaceous limestone ("cement rock") ground in open circuit in a commercial-type combination tube mill. Dispersion and calibration as in sample LS. Specific gravity of material, 2.62. Sample RL.—Cement Reference Laboratory No. 3 high-early-strength cement. Dispersion effected by modified procedure. Instru-



Figs. 3 to 13.—Eleven Samples of Materials ranging in fineness from Crushed Clinker from P.C.A. Testing Apparatus to High-Early-Strength Cements and two Raw Materials.

ment calibrated by "mask" method. Sample TS.—A "tailings" product from a closed-circuit grinding operation. Dispersion effected by a modified procedure and instrument calibrated by "mask" method. Sample GN.—A product from a single-roll and ring preliminary-type pulveriser. Dispersion effected by modified procedure and instrument calibrated by "mask" method. Sample BC.—A product from a 3-roll and ring preliminary-type pulveriser. Dispersion and calibration by standard procedure. Sample GB.—A crushed clinker produced by a Portland Cement Association grindability testing apparatus.

TABLE III.—PARTICLE SIZE DISTRIBUTIONS, SURFACE MEAN DIAMETERS AND SURFACE AREAS, BASED ON TURBIDIMETRIC ANALYSES.

Sample	LG	HC	HO	LS	CR	RL	TS	GN	BC	GB	SS
(0-7.5)	3.75	3.75	3.75	3.75	3.75	3.75	3.75	3.75	3.75	3.75	3.75
55 $\mu$	100.	100.	100.	100.	100.	100.	100.	100.	100.	100.	100.
50	98.1	100.	98.5	98.1	98.9	100.	93.5	98.5	93.6	92.1	96.4
45	95.8	100.	97.9	95.4	96.9	99.2	82.9	93.3	85.5	82.0	92.5
40	93.1	98.6	95.4	92.3	94.2	98.4	73.3	86.2	80.3	72.9	87.9
35	87.7	93.6	93.7	89.0	90.3	96.0	58.7	80.4	73.5	62.4	82.8
30	79.3	89.4	91.8	84.3	88.9	91.8	47.3	72.4	66.0	52.6	77.0
25	74.0	81.3	81.5	79.7	82.8	84.3	37.7	60.2	57.0	42.0	70.6
20	67.1	69.6	70.3	73.1	76.7	73.8	29.8	50.9	46.9	29.9	62.3
15	56.6	58.7	56.9	66.8	68.6	58.3	26.4	40.0	35.2	21.6	52.5
10	44.9	42.0	43.2	57.8	57.1	41.2	19.8	26.7	22.9	11.9	39.2
7.5	38.5	34.5	36.0	52.6	49.5	31.8	16.7	20.6	16.2	8.1	30.9
$\Sigma d_m$	7.39	7.62	7.40	6.04	6.18	7.83	13.4	10.6	12.0	17.0	8.31
$SA_g$	2585	2500	2575	3625	3705	2430	1415	1800	1590	1125	2285
-325	95.7	99.2	98.5	68.1	81.6	99.8	59.0	58.5	33.5	14.0	88.9
$SA_n$	2475	2180	2335	2470	3025	2425	835	1055	530	157	2030
(0-7.5)	2.90	3.30	3.20	2.22	2.51	3.42	3.04	3.73	4.00	4.50	3.28
55 $\mu$	100.	100.	100.	100.	100.	100.	100.	100.	100.	100.	100.
50	98.0	100.	98.5	97.6	98.7	100.	93.3	96.5	93.7	91.2	96.2
45	95.6	100.	97.7	94.2	96.3	99.2	82.2	93.3	85.7	82.2	92.1
40	92.6	98.4	95.1	90.3	93.1	98.5	72.2	86.2	80.6	73.1	87.3
35	86.6	93.4	93.3	85.9	88.4	96.0	57.1	80.4	73.8	62.9	82.0
30	77.4	89.0	91.2	79.9	84.3	91.7	45.4	72.4	66.4	53.3	76.0
25	71.6	80.5	80.4	74.1	79.4	83.9	35.5	60.2	57.5	42.8	69.4
20	64.1	68.2	68.6	65.8	72.1	73.1	27.4	50.9	47.5	30.9	60.7
15	52.6	56.9	54.5	57.7	62.4	57.1	23.9	40.0	35.9	22.8	50.5
10	39.7	39.5	40.1	46.4	48.7	39.5	17.1	26.6	23.7	13.3	36.7
7.5	32.6	31.7	32.5	39.6	39.6	29.8	13.9	20.5	17.1	9.6	28.1
$\Sigma d_m$	6.71	7.31	7.01	4.75	5.16	7.61	13.0	10.6	12.1	17.2	8.02
$SA_g$	2835	2605	2715	4610	4435	2505	1465	1800	1570	1110	2375
-325	95.7	99.2	98.5	68.1	81.6	99.8	59.0	58.5	33.5	14.0	88.9
$SA_n$	2715	2585	2675	3140	3620	2500	865	1055	525	155	2110

Note. In the above Table, Particle Size Distributions are Gross. To find Net values multiply by 325-mesh finenesses.

$\Sigma d_m$  = Surface Mean Diameters of the (0-55) micron fraction.

$SA_g$  = Gross Surface Areas of the (0-55) micron fraction.

-325 = Fineness of material passing a 325-mesh sieve.

$SA_n$  = Net Surface Areas of the minus 325 mesh fraction.

Dispersion by modified procedure. Instrument calibrated to  $I_0 = 31.6$ . Sample SS.—A standard cement sample (U.S. Bureau 114b). Dispersion by modified procedure. Instrument calibrated by "mask" method.

#### Effect on Various Materials of Different Grinding Methods.

It is interesting to note from Table III how the recalculated (0-7.5) micron fraction affects the particle size distributions, surface mean diameters, and surface areas. A decrease in the average (0-7.5) micron fraction decreases the value of

the percentage less than 7.5 microns, decreases the surface mean diameters, and increases the surface areas.

In comparing samples LG, HC, and HO, the ordinary analysis shows that the surface areas are about the same. However, by the modified analysis LG shows a much higher surface area due to the fact that the average 0.75 micron fraction is smaller. HO in comparison with HC shows a difference of 55 sq. cm. per gramme for the ordinary analysis and 90 sq. cm. per gramme for the modified analysis. This difference could easily account for a difference in strength producing characteristics of a cement ground in open circuit as against a similar cement ground in closed circuit to practically the same fineness as shown by the ordinary methods.

Sample LG shows a relatively high surface area but a rather peculiar gradation. The 0.75 fraction is fairly high but the gradation up to 30 microns is decidedly low in comparison with similar types of cement ground in open circuit, as HO. It is generally recognised that laboratory-ground cements do not perform in the same manner as commercial products. An examination of the particle size distributions may throw some light on the reason for these apparent differences.

Samples LS and CR are especially interesting because they show the grading characteristics of cement raw materials. While LS is considered a very hard grinding limestone it nevertheless shows a higher fineness, in terms of surface mean diameters, than the comparatively easy grinding cement rock. Experience with the grinding of these materials shows that material CR breaks down readily and it is not especially difficult to eliminate critical particle size in terms of plus 100-mesh material. On the other hand, sample LS is resistant to the elimination of critical particle size. Both these materials should respond readily to air classification and thus reduce the problem of oversize material without an undue amount of minus 0.75 micron material which could be very easily lost during the burning process.

An air elutriation analysis showed that sample LS had 29.3 per cent. less than 10 microns and sample CR had 41.3 per cent. less than 10 microns. The Wagner analysis with the calculated 0.75 micron fraction showed 31.6 per cent. for sample LS and 39.6 per cent. for sample CR. On the other hand the Wagner analysis without any modifications showed 39.4 per cent. for sample LS and 46.6 per cent. for sample CR. Sample RL is included because of the interest shown in this material at the present time.

Sample TS is a "tailings" product from a closed-circuit grinding operation. This material is especially interesting because it shows a "primary" and "secondary" distribution function. In an analysis of this type it is necessary to determine the distribution function at or near 7.5 microns and substitute the value for  $d_{m7.5}$  in equation (4) and thus calculate the surface area. Sample TS may be considered as "dirty" tailings, i.e. it contains a relatively large amount of 0.75-micron material. The modified analysis may thus be useful in analysing the performance of air separators and closed-circuit grinding in general. Samples GN and BC are similar to sample TS in that a "primary" and "secondary"



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distribution function is shown. These materials are relatively coarse so that a modification of the Wagner analysis does not show any great difference.

Sample GB is about the coarsest material subjected to Wagner analysis. Here again is found a "primary" and "secondary" reduction function. Sample SS is "standard" sample 114b. In the analysis in Table III the distribution function has been considered normal with the equation defined by a single parameter.

In ordinary cement grinding, with either open or closed circuits, normal distribution functions will be encountered. Naturally the law of turbidity versus particle size will not hold for abnormal distributions. Conversely, the ordinary Wagner analysis will fail, and it is therefore necessary to resort to other methods of fineness determinations.

Frequently, it will be found that particulate materials break down into a "primary" and "secondary" distribution function. It is therefore necessary to treat these functions separately. In this category are the products of coarse crushing and grinding operations and possibly some air-separated materials. Finely-ground products usually assume a normal distribution with a complete analysis determined from a single equation. In fact some of the more finely divided materials, such as high-early-strength cements, plot to the normal distribution function better than the coarser products. This fact is important because in the analysis of grindability and grinding plant equipment computations for efficiency are highly speculative in the greater fineness range. Perhaps the grinding equipment is not so inefficient after all, and what may have been considered low efficiencies in operation may be accounted for by lack of precision of the amount of new surface created during pulverisation, or failure to establish accurately the standard grindability factor upon which efficiency must be calculated.

#### REFERENCES

- (1) Wagner, L.A.: A Rapid Method for the Determination of the Specific Surface of Portland Cement, *Proc. Am. Soc. Test. Mat.*, 33, Part II, pp. 553-70 (1933).
  - (2) Traxler, R. N. and Baum, L. A. H.: Measurement of Particle Size Distribution by Optical Methods. *Proc. Am. Soc. Test. Mat.*, 35, Part II, 457-71 (1935).
  - (3) Fritts, S. S.: Average Diameter of Particles Just Passing the 325-mesh Sieve. *Ind. and Eng. Chem., Analytical Edition*, Vol. 9, 180, April 15, 1937.
  - (4) Wilson, R.: A Method for Estimating the Efficiency of Pulverizers. *A.I.M.E. Tech. Pub.*, 810 (1937).
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## New Method for Determining the Alkali Content of Cement.

A METHOD for the rapid determination of alkalis in Portland cement, which needs about one-third of the time required by the tentative method of the American Society for Testing Materials, is suggested by Mr. F. W. Glaze (of the United States National Bureau of Standards) in a recent number of *Rock Products*. In this method, the sample of cement is decomposed by hydrofluoric acid in the presence of nitric and perchloric acids, and the resulting perchlorates are decomposed by gentle ignition. The alkalis are determined in the extract from the ignited residue, the sodium as uranyl zinc sodium acetate, and the potassium from the platinum in the chloroplatinate precipitate. The advantages claimed for this method are its speed and simplicity and, so far as it has been tried, there is said to be no material sacrifice of accuracy.

In describing the new method the author states that the effects of the sodium and potassium oxides normally present in Portland cement on the properties of the cement have been receiving considerable attention recently. The present indications are that their effect is considerable because of their tendency to form complex molecules.<sup>1</sup> Also, the State of California has already limited the amount of total alkali that may be present in cement used for highway construction with certain aggregates to 0.5 per cent. when calculated as sodium oxide. The A.S.T.M. Committee C-1 on cement has recommended a method which requires the treatment of a 5-g. sample of cement by a modified J. Lawrence Smith procedure. The total alkalis are weighed as sulphates, the potassium is determined as the chloroplatinate, and the amount of sodium obtained by difference. This method seems needlessly long and involved because of the digestions and numerous filtrations necessary to extract the alkalis from the sinter and to purify the alkali extract. After studying this above method and other possible procedures that would require less time and attention, the method described was tried and found to be satisfactory.

### The Method.

To 1 g. of cement in a platinum dish, add 5 ml. of distilled water, stir to break up any lumps that form and then carefully add 5 ml. of  $\text{HNO}_3$  (sp. gr. 1.42). Stir with a platinum rod until decomposition is complete. Now add 5 ml. of  $\text{HClO}_4$  (60 per cent.) and 15 ml. of  $\text{HF}$  (48 per cent.), thoroughly mix by stirring with the platinum rod, and evaporate to fumes of  $\text{HClO}_4$  over a radiator<sup>2</sup> or air bath.<sup>3</sup> Cool, remove the rod, wash down the sides of the dish with distilled water, evaporate, and fume off the excess  $\text{HClO}_4$ . Ignite the residue gently over a free flame (with the dish covered) to decompose the perchlorates, at no time allowing the temperature to exceed 500 deg. C. (incipient redness). Cool, add 50 ml. of distilled water, crush all lumps with the flattened end of a stirring rod, digest on the steam bath for 30 minutes, filter through a 9-cm. paper (Whatman No. 42 or equivalent) and wash 20 times with hot distilled water.

using about 3 ml. each time. The filtrate and washings should amount to about 125 ml. Acidify the filtrate with HCl (1 : 1), evaporate to about 75 ml. in glass, cool, transfer to a 100-ml. volumetric flask and take 10 ml. for the  $\text{Na}_2\text{O}$  determination and reserve the remaining 90 ml. for the  $\text{K}_2\text{O}$ .

**Sodium Oxide.**—The  $\text{Na}_2\text{O}$  is determined as uranyl zinc sodium acetate.<sup>4</sup> Evaporate the 10-ml. aliquot sample in a small beaker or casserole to dryness on a steam bath. Cool to room temperature, take up the residue in 1 ml. of distilled water, and add 10 ml. of the uranyl zinc acetate reagent.<sup>5</sup> After standing for two hours, filter through a weighed glass filter crucible by suction. A 30-ml. Jena crucible (1bG3) or its equivalent has been found satisfactory. Wash the precipitate by decantation five times with the precipitating reagent (using 2 ml. each time), transfer the precipitate to the crucible with ethyl alcohol which has been saturated with the sodium salt and to which 1 per cent. by volume of acetic acid has been added, then wash ten times with the alcohol wash solution (using about 2 ml. each time), and finally three times with ether. Draw air through the crucible until the odour of ether is removed, wipe off the outside of the crucible with a damp cloth to avoid electrostatic effects, place the crucible in a desiccator for about ten minutes, and then remove to the balance case. Weigh as soon as the crucible and contents reach constant weight (after about 15 minutes in the balance case).

$$\text{Per cent. Na}_2\text{O} = \frac{\text{wt. of precipitate} \times 0.02051 \times 100}{0.1}$$

**Potassium Oxide.**—The  $\text{K}_2\text{O}$  is determined by the modified chloroplatinate method.<sup>6</sup> To the 90-ml. aliquot sample, transferred to a small casserole (or beaker), add an amount of chloroplatinic acid solution slightly in excess of that necessary for the complete precipitation of the potassium present and evaporate on a steam bath to a syrupy consistency, i.e. until solidification occurs on cooling. Drench the cooled residue with about 2 ml. of ethyl alcohol (80-85 per cent. by volume), break up the residue with the flattened end of a stirring rod, and allow to stand for half an hour. The alcohol solution should be coloured if an excess of chloroplatinic acid has been used. Pour the liquid through a small filter paper (Whatman No. 42 or equivalent). Wash by decantation four more times, pouring off the liquid each time as soon as the filter drains, and finally wash around the top of the filter three times. Transfer the  $\text{K}_2\text{PtCl}_6$  in the casserole to a 250-ml. beaker and wash the casserole and the filter with hot water (receiving the washings in the 250-ml. beaker), adjust the volume to about 100 ml., and warm on the steam bath to dissolve the  $\text{K}_2\text{PtCl}_6$ . Add 1 ml. of HCl (sp. gr. 1.18) and about 0.5 g. of magnesium ribbon wrapped around the end of a stirring rod and continue to digest on the steam bath. When the action ceases or the solution becomes cloudy because of the formation of basic magnesium salts, add 2 ml. of HCl (sp. gr. 1.18). When the platinum settles and the supernatant liquid is clear, add 2 ml. more of HCl (sp. gr. 1.18), boil for several minutes, filter, and

wash twenty times with hot water. The paper and platinum are then ignited to constant weight in a weighed porcelain crucible.

$$\text{Per cent. K}_2\text{O} = \frac{\text{wt. of Pt} \times 0.4825 \times 100}{0.9}$$

Careful blanks should be run on all the reagents used, following exactly the same procedure as used in the analysis. It should be possible, using this method, to determine the sodium and potassium in a sample of cement in a 7-hour day as compared with a minimum of three days required by the A.S.T.M. method.

### Results.

The following table gives some results obtained by this method in comparison with results obtained by other methods:

	Per cent. Na <sub>2</sub> O		Per cent. K <sub>2</sub> O	
	Glaze	Others	Glaze	Others
Comparative sample No. 3 (1) .....	0.39	0.33 (2)	0.23	0.23 (2)
Clinker No. 6 .....	0.70	0.62 (3)	0.50	0.52 (3)
Clinker No. 9 .....	0.79	0.81 (4)	0.00	0.08 (4)

(1) Cement Reference Laboratory sample. (2) Averages obtained by co-operators using the A.S.T.M. tentative method. (3) A.S.T.M. tentative method, by J. J. Tregoning. (4) J. Lawrence Smith method (1-g. sample, and determining both Na<sub>2</sub>O and K<sub>2</sub>O), by J. J. Tregoning.

<sup>1</sup> Unpublished data of Insley and McMurdie, and of the Portland Cement Association Fellowship.

<sup>2</sup> Construction and use of radiators are described on p. 33 of W. F. Hillebrand's "The Analysis of Silicate and Carbonate Rocks" (Bulletin 700 of the Department of the Interior) and on p. 22 of Hillebrand and Lundell's "Applied Inorganic Analysis."

<sup>3</sup> A suitable air bath is shown in Fig. 26 on p. 47 of Treadwell and Hall's "Analytical Chemistry," Vol. II (seventh edition).

<sup>4</sup> Barber and Kolthoff, *J. Am. Chem. Soc.* 50, 1625 (1928). Glaze, *J. Am. Ceram. Soc.*, 14, 450 (1931).

<sup>5</sup> This reagent is prepared from the following solutions:

Solution A	Grams
Uranyl acetate (2H <sub>2</sub> O) .....	10
Acetate acid (30%) .....	6
Water to make .....	65

Solution B	Grams
Zinc acetate (3H <sub>2</sub> O) .....	30
Acetate acid (30%) .....	3
Water to make .....	65

After solutions A and B have been prepared (by warming), they are mixed while warm and allowed to stand for 24 hours. A precipitate of uranyl zinc sodium acetate usually forms from the small amount of Na<sub>2</sub>O in the chemicals used. If no precipitate forms, add (with stirring) a small crystal of NaCl and allow to stand for two hours. Repeat until a definite yellow crystalline precipitate is obtained, thus ensuring saturation of the reagent with the triple salt at room temperature. In either case the precipitate is filtered off. When kept in Pyrex glass the reagent does not become turbid after long standing.

<sup>6</sup> Hicks, *J. Ind. Eng. Chem.* 5, 650 (1913).